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FORBIDDEN ABSORPTION BANDS OF O_2 IN THE ARGON CONTINUUM REGION[1]

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The absorption spectrum of O_2 has been photographed in the argon continuum region by a 3-m vacuum spectrograph with a dispersion of 1.42Å/mm. Using the known rotational constants of the ground state, the rotational constants of the upper states of the Tanaka progression (I); $\beta - X\,^3\Sigma_g^-$, progression (II); $\alpha\,^1\Sigma_u^+ - X\,^3\Sigma_g^-$, and those of a new band at 1144.6Å have been determined. Brief discussions for the upper electronic states are presented and it is suggested that both the β state and the upper states of the 1144.6Å band are $^3\Sigma_u^+$ states and their electron configurations are $(\pi_g 2p)(3p\pi)$ and $(\pi_g 2p)(4p\pi)$, respectively.

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INTRODUCTION

The absorption spectrum of O_2 in the region from 1000 to 1350Å has been studied by Price and Collins (1935) and by Tanaka (1952). They reported many strong absorption bands, and Tanaka has classified weak bands into two progressions, (I) and (II). However, there was no report of the rotational analysis of any band in this region before the recent work carried out by Alberti, Ashby, and Douglas (1968). They observed a number of new absorption bands of the excited O_2 (a $^1\Delta_g$, and b $^1\Sigma_g^+$) and analyzed the rotational structures of some new bands in addition to the progressions (I) and (II). They have also assigned these two progressions to the $\beta\ ^1\Sigma_u^+ - X\ ^3\Sigma_g^-$ system and the $\alpha\ ^1\Sigma_u^+ - X\ ^3\Sigma_g^-$ system, respectively. Independently, we analyzed the rotational structures of the progressions (I) and (II), and a new band at 1144.6Å.

EXPERIMENTAL PROCEDURES

A 3-m vacuum spectrograph equipped with a grating of 1200 lines/mm blazed at 2950Å was used. Its reciprocal linear dispersion was 1.42 Å/mm in the second order. An argon emission continuum (1100-1500Å) was used as a background. In order to obtain the continuum, argon gas was continuously flowed through a water cooled Π-shaped discharge tube with a LiF window and was excited by a neon

sign transformer, 900 W, 15 kV, in combination with a 500μμF capacitor and a 3-mm air-blown spark gap. The argon pressure was maintained at about 18 Torr. Spectra were taken with Kodak SWR plates.

The spectrograph itself was used as an absorption cell whose path length was 6 meters. Extra-dry oxygen gas, obtained from the Matheson Co., was introduced into the spectrograph and caused to flow continously. The pressure of the oxygen gas was kept almost constant at the various pressures between 5 and 500μ.

RESULTS

The absorption spectrum showed many very complex features. At the present dispersion the bands, whose rotational structure could be analyzed, were limited to the following ones; the 1262.1 and 1233.4Å bands of the progression (I), the 1250.0, 1222.1, and 1196.1Å bands of the progression (II), and a new band at 1144.6Å. All these bands show the same structure; double heads, three branches, and shading toward shorter wavelength. Enlarged spectra of the 1144.6Å band and the 4-0 band of the α-X system are shown in Fig. 1. Observed wave numbers and assignments of the rotational lines are listed in Tables I, II, and III. All bands consist of three branches corresponding to $\Delta N=0, \pm 2$ and only the rotational lines with odd N' (upper state) have been observed. This suggests that the upper state is one

of the $^1\Sigma_g^-$, $^3\Sigma_g^-$, $^1\Sigma_u^+$, and $^3\Sigma_u^+$ states. The transition between any of these states and the $X\,^3\Sigma_g^-$ ground state is forbidden.

The processes of the analysis of the bands were the following. Firstly, the Δ_2F'' values which agreed with the known Δ_2F values of the $X\,^3\Sigma_g^-$ state were found by means of the combination relation (Herzberg's book, pp 175-185, 1950). Secondly, according to this result and the Δ_2F' curve, the quantum numbers of the rotational lines, N' and N'', were determined. Thirdly, the values of ν_o, B', and D' were obtained from the observed wave numbers of all the lines and the equation,

$$\nu_{N'N''} = \nu_o + B'N'(N'+1) - D'N'^2(N'+1)^2 - B''N''(N''+1) + D''N''^2(N''+1)^2.$$

Observed Δ_2F'' values of all bands agreed well with the Δ_2F_2'' values of the v=0 level of the $X\,^3\Sigma_g^-$ ground state, observed with a high resolution spectrograph by Babcock and Herzberg (1948). An example for the 1144.6Å band can be seen in Table III. Therefore, the values $B'' = 1.4378\ cm^{-1}$ and $D'' = 4.913 \times 10^{-6}\ cm^{-1}$ for the F_2 rotational levels, given by Babcock et al., were used in the above formula. The values of ν_o, B', and D' thus obtained are listed in Table IV.

According to Babcock et al., the separations of the rotational sublevels, F_3-F_1, of the v=0 of the $X\,^3\Sigma_g^-$ state are less than $0.47\ cm^{-1}$ between N=3 and 29, and the average positions of F_1 and F_3 are

2.009 cm^{-1} lower than the F_2 levels. Therefore, the rotational constants, B′ and D′, determined from the above formula are fairly accurate regardless of whether the upper state is a singlet or a triplet state. However, when an upper state is a $^1\Sigma_u^+$ state, there will be no transition from the F_2 sublevel of the ground state, and the observed lines are due to transitions from the F_1 and F_3 sublevels. Therefore, the ν_o values which are obtained from the formula mentioned above need a correction to give the true values which are measured from the $F_2(0)$ level and are 2.0 cm^{-1} smaller. The ν_o values thus corrected are listed for the $\alpha\ ^1\Sigma_u^+ - X\ ^3\Sigma_g^-$ system in Table IV. The present analysis was carried out by including the rotational constant D′, which was not considered in the previous work. As a consequence, the present B′ values are larger than previous values (see Table IV and Fig. 4).

(a) progression (II), $\alpha\ ^1\Sigma_u^+ - X\ ^3\Sigma_g^-$

According to Alberti et al., the upper state of the progression (II) is definitely a $^1\Sigma_u^+$ state and has been called the $\alpha\ ^1\Sigma_u^+$ state. Rotational lines of the (3-0) band at 1222.1Å and the (4-0) band at 1196.1Å are sharp, but those of the (2-0) band at 1250.0Å are rather diffuse. Except for the (4=0) band, the observed wave numbers of the rotational lines agree well with those measured by Alberti et al. with a high resolution spectrograph. The wave numbers of all the rotational

lines of the (4-0) band of the present measurements are larger by about 13.5 cm^{-1} than those measured by them. However, Douglas (1968)* has corrected their published values, and these corrected values are also listed in Table I. As seen in the table, the present values agree well with the corrected ones except for the $^{o}P(13)$ line.

The (4-0) band shows rotational perturbation. Observed shifts of the rotational levels of v=4 of the $\alpha\ ^{1}\Sigma_{u}^{+}$ state are shown in Fig. 2. Three levels are perturbed. The levels with N = 7 and 9 shift downward, 0.3 and 2.1 cm^{-1} respectively, while the level with N = 11 shifts 1.3 cm^{-1} upward. In order to yield such shifts, a rotational constant of a perturbing vibrational level must be smaller than that of the v = 4 level of the $\alpha\ ^{1}\Sigma_{u}^{+}$ state.

The $^{o}P(13)$ line corresponds to the transition from N″ = 13 to N′ = 11. However, this line overlaps accidentally with the $^{o}P(11)$ line, because both N′ = 9 and 11 are shifted by rotational perturbation. The line assigned as $^{o}P(13)$ by Alberti et al. must be the $^{o}P(15)$ line, then its wave number agrees well with the present one.

(b) progression (I), $\beta - X\ ^{3}\Sigma_{g}^{-}$.

The 1262.1Å and 1233.4Å bands of the progression (I) could be analyzed in the present work. These bands are very diffuse.

*According to the private communication of Dr. A. E. Douglas, the published values resulted by adding accidentally the vacuum correction onto each line as if there were air in the spectrograph when the wave numbers were calculated by a computer.

However, we were able to observe the first lines of the S- and Q-form branches and were also able to observe more of their higher members than in the previous work by changing the pressure of O_2 and the exposure times. The observed wave numbers listed in Table II agree well with those observed by Alberti et al. The upper state has been temporarily assigned to be $\beta\ ^1\Sigma_u^+$ by Alberti et al. However, we favor it to be the $\beta\ ^3\Sigma_u^+$ state. More details on this will be given in the discussion section.

(c) 1144.6Å band

When the O_2 pressure was higher than 200μ, a very weak band whose appearance was very similar with those of the progressions (I) and (II) was newly observed at 1144.6Å (Q-form head). This band was located in one of the transmission windows whose absorption coefficient is 0.31 cm^{-1} (Metzger and Cook, 1964). An enlarged photograph of this band is shown in Fig. 1. Lines of S- and Q-form branches are sharp, while the lines of O-form branch are diffuse because of blending with other lines including H_2O impurity lines. The observed wave numbers and the Δ_2F values are listed in Table III. The Δ_2F values obtained from a Q-O combination relation are not accurate compared with those obtained from an S-Q combination relation. This can be seen in Table III by comparing the Δ_2F'' values, obtained by these two combinations, with the Δ_2F_2'' values obtained by

Babcock and Herzberg. An upper electronic state is suggested as a $^3\Sigma_u^+$ state (see the discussion section).

DISCUSSION

As an example of the $\Delta_2 F'$ values, the $\Delta_2 F'$ curve of the 1144.6Å band (5th column of Table III) is shown in Fig. 3, and the curve is described by a formula,

$$\Delta_2 F(N) = 4B\,(N+\tfrac{1}{2}) - 8D\,(N+\tfrac{1}{2})^3 ,$$

where the rotational quantum numbers N are even numbers. This means that O_2 molecules are in rotational levels described by the odd N numbers. This is the case for all upper states of the bands presently analyzed. O_2 molecules are in those rotational levels which must be symmetric with respect to an exchange of the two nuclei. Therefore, the possible upper electronic state which gives the symmetric rotational levels with odd N numbers is a $^1\Sigma_g^-$, $^3\Sigma_g^-$, $^1\Sigma_u^+$, or $^3\Sigma_u^+$ state.

The observed rotational constants of the upper states of all bands are slightly larger than those of the $X\ ^2\Pi_g$ ground state of O_2^+ (see Fig. 4). If we consider these rotational constants and the vibration quanta of the upper states together with the location of the bands, the upper states must be the Rydberg states which converge to the $X\ ^2\Pi_g$ ground state of O_2^+ as suggested by Alberti et al. Possible electron configurations are:

$(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)(np\pi)$, for $^1\Sigma_u^+$ and $^3\Sigma_u^+$

and $(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)(nd\pi)$, for $^1\Sigma_g^-$ and $^3\Sigma_g^-$.

As mentioned earlier, the α state is definitely a $^1\Sigma_u^+$ state (Alberti et al.). We suggest that the electron configuration of the α $^1\Sigma_u^+$ state is $(\pi_g 2p)(3p\pi)$ which may also be written as $(\pi_g 2p)(\pi_u 3p)$, the lowest member of the $(\pi_g 2p)(np\pi)$ series. This configuration assignment has been made for two reasons: firstly, because the effective quantum number of the α $^1\Sigma_u^+$ state is 2.285 and, secondly, because the observed vibrational and rotational constants of the α $^1\Sigma_u^+$ state are slightly larger than those of the $X^2\Pi_g$ state, and the 3pπ or $\pi_u 3p$ electron is a bonding electron.

An ndπ electron is nonbonding or slightly antibonding and, specifically, a 4dπ or $\pi_g 3p$ electron is antibonding. Therefore, one cannot expect a $^1\Sigma_g^-$ state or a $^3\Sigma_g^-$ state, derived from the $(\pi_g 2p)(nd\pi)$ configuration, to have rotational constants or the vibrational constants which are larger than those of the $X^2\Pi_g$ state. We suggest that the β state is a $^3\Sigma_u^+$ state instead of a $^1\Sigma_u^+$ state which was suggested by Alberti et al.. The rotational constant of the upper state of the 1144.6Å band is 1.706 cm^{-1}, which is the largest one among all bands analyzed in the present work. The upper state of this band is probably a $^3\Sigma_u^+$. The electron configurations of the β state and the upper state of the 1144.6Å band are $(\pi_g 2p)(3p\pi)$ and $(\pi_g 2p)(4p\pi)$, respectively. The

$\alpha\ ^1\Sigma_u^+$ and $\beta\ ^3\Sigma_u^+$ states are the singlet-triplet pair states with the $(\pi_g 2p)(\pi_u 3p)$ configuration.

The intensity of the 1144.6Å band is weaker than the 1-0 band of the α-X system. Here the vibrational quantum numbers of the upper state of the 1144.6Å band and the 1262.1Å band of the β-X system are tentatively assigned as v=0 and 2, respectively. According to this assignment, the B curves of the upper state of the 1144.6Å band and the β state are shown in Fig. 4. The 0-0 band of the β-X system† is expected at around 75450 cm^{-1}, 1325.4Å (n^*=2.241), which is about 790 cm^{-1} lower than that of the α-X system. As seen in Fig. 4, these B values are lying on nearly the same line. Lindholm (1968) has also suggested that the β state is a $^3\Sigma_u^+$ state.

†The 1-0 band of the β-X system has been observed at 1292.5Å (77368 cm^{-1}) by Tanaka (1952). He assigned this band to the first band of the progression (I). Alberti et al. could not observe it even on their good plates. However, in the present study, this band was easily seen, when the O_2 pressure was 50- 100μ, and it faded out into a 1290Å continuum at higher pressures. This band is very diffuse, does not show any rotational structure, and overlaps with a continuum. A band of this type is difficult to detect at very high resolution.

REFERENCES

Alberti, F., Ashby, R.A., and Douglas, A.E. 1968. Can J. Phys. 46, 337.

Babcock, H.D. and Herzberg, L. 1948. Astrophys. J. 108, 167.

Douglas, A.E. 1968. Private communication.

Herzberg, G. 1950. Molecular Spectra and Molecular Structure, I (D. Van Nostrand Co. Inc., New York).

Lindholm, E. 1969. Private communication; to be published in Arkiv Fysik.

Metzger, P.H. and Cook, G. R. 1964. J. Quant. Spectrosc. Radiat. Transfer, 4, 107.

Price, W.C. and Collins, G. 1935. Phys. Rev. 48, 714.

Tanaka, Y. 1952. J. Chem. Phys. 20, 1728.

FIGURES

Fig. 1: The absorption spectra of the 4-0 band of the α-X system and the 1144.6Å band.

Fig. 2: Rotational perturbation of the v=4 level of the $\alpha\ ^1\Sigma_u^+$ state.

Fig. 3: The Δ_2F' curve of the 1144.6Å band.

Fig. 4: Rotational constants of the α and β states, and the upper state of the 1144.6Å band.

TABLES

Table I : Wave numbers of the lines of the $\alpha\ ^1\Sigma_u^+ - X\ ^3\Sigma_g$ system.

Table II: Wave numbers of the lines of the $\beta\ ^3\Sigma_u^+ - X\ ^3\Sigma_g^-$ system.

Table III: Wave numbers and Δ_2F values of the 1144.6Å band.

Table IV: Forbidden absorption bands of O_2.

TABLE I

Wave Numbers of the Lines of the $\alpha\ ^1\Sigma_u^+ - X\ ^3\Sigma_g^-$ System

	2 - 0 band			3 - 0 band		
N	^sR	$^QR+^QP$	^oP	^sR	$^QR+^QP$	^oP
1	80021.4	80004.3*	-	81841.8	81825.3	-
3	035.0	004.3*	79988.9	856.3	827.7	81810.6
5	052.5	009.4	979.8	872.9	830.4	800.9
7	070.4	014.9	971.5	890.9	835.3	793.1
9	091.0	021.7	964.5*	910.5	846.8	786.6*
11	112.9	030.5	959.1*	931.6*	850.0	781.8*
13	136.2	041.7	959.1*	954.0	860.3	777.0*
15	161.3	052.5	959.1*	978.5	870.7	777.0*
17	189.1	065.3	959.1*	82004.0	883.8	777.0*
19		082.7		031.7	898.8	777.0*
21				060.9		781.8*
23				088.5	931.6*	
25				125.0		
27				155.5		
29				190.0		

	4 - 0 band			4 - 0 band (Douglas)**		
N	^sR	$^QR+^QP$	^oP	^sR	$^QR+^QP$	^oP
1	83618.5*	83602.0	-	83617.81*	83601.85	-
3	632.8*	603.6	83587.6	632.50*	603.67	83587.64
5	648.8	606.7	578.1	648.02	606.54	577.70
7	664.2	611.0	569.7	663.45	610.68	569.17
9	686.2	615.7	562.2*	685.74	614.66	561.79
11	705.3	625.8*	554.5*	704.95	625.34*	553.91
13	726.5	632.8*	554.5*		632.50*	549.29
15	749.5	643.2	548.8*			
17		654.8	548.8*			
19			548.8*			

*Unresolved blend with other line.

**Wave numbers published previously (Alberti, Ashby, and Douglas; 1968) have been corrected as shown in this Table. Private communication of Douglas.

TABLE II

Wave Numbers of the Lines of the $\beta\ ^3\Sigma_u^+ - X\ ^3\Sigma_g^-$ System

	1262.1Å band			1233.4Å band		
N	S-form	Q-form	O-form	S-form	Q-form	O-form
1	79249.7*	79230.7*	-	81091.5	81072.6	-
3	258.8*	230.7*	79214.7	106.4*	075.4	81060.2
5	279.7*	236.7	206.4	121.4*	080.0	050.9
7	298.5*	242.0*	197.8*	140.9	085.4	042.5
9	319.9	249.7*	187.6*	160.2	091.5	036.1
11	340.5	258.8*	187.6*	180.8	100.4	031.4
13	363.4	271.5	187.6*	203.5	110.2*	028.0*
15	388.5	279.7*		228.2	121.4*	026.5*
17	416.0	298.5*		254.0	134.5	026.5*
19	450.0	313.7		280.0	149.4	
21				308.0		

*Unresolved blend with other line.

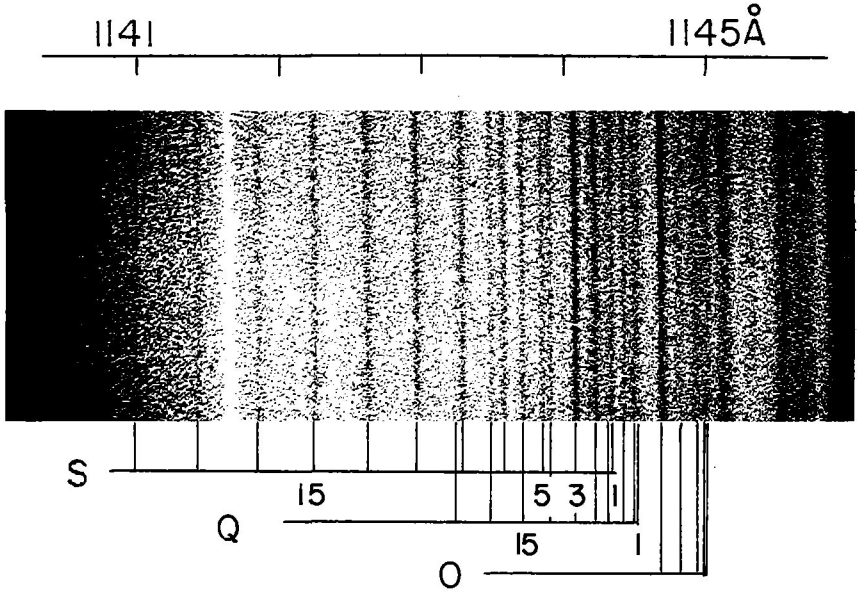
TABLE III

Wave Numbers and $\Delta_2 F$ values of the 1144.6Å Band

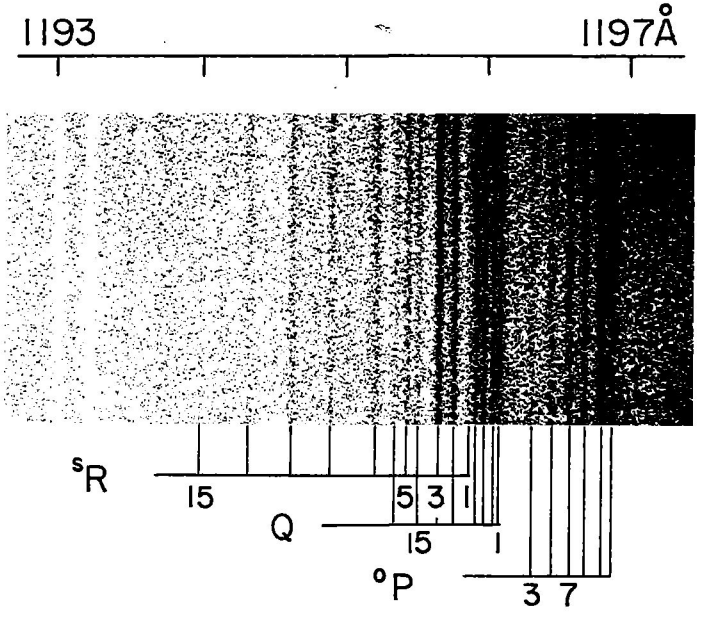
				$\Delta_2 F'$		$\Delta_2 F''$		
N	S-form	Q-form	O-form	S-Q	Q-O	S-Q	Q-O	B & H**
1	87386.7*	87368.7	-	18.0	14.8	14.7	11.5	14.37
3	403.4	372.0	87357.2*	31.4	29.6	25.7	23.9	25.88
5	421.6	377.7	348.1*	43.9	44.6	37.2	37.9	37.37
7	441.9	384.4	339.8*	57.5	59.7	48.9	51.1	48.86
9	464.5	393.0*	333.3*	71.5	70.1	61.1	59.7	60.34
11	488.7	403.4*	333.3*	85.3	84.0	71.4	70.1	71.81
13	515.1	417.3	333.3*	97.8	98.5	83.3	84.0	83.27
15	543.7	431.8	333.3*	111.9	109.2	94.7	92.0	74.72
17	574.3	449.0	339.8*	125.3	127.2	107.3	109.2	106.15
19	606.3	467.0	339.8*	139.3			118.9	117.56
21	641.3		348.1*					
23	677.0							

*Unresolved blend with other line.

**Babcock and Herzberg (1948).



1144.6Å Band, $^3\Sigma_u^+ - X\,^3\Sigma_g^-$



4-0 Band, $a\,^1\Sigma_u^+ - X\,^3\Sigma_g^-$

Fig. 1

TABLE IV

Forbidden Absorption Bands of O_2

	Assignment		Present			Alberti et al.	
λhead(Å)	Electronic	v′-v″	$\nu_o(cm^{-1})$	$B'(cm^{-1})$	$D'(cm^{-1})$	$\nu_o(cm^{-1})$	$B'(cm^{-1})$
1250.0Q	$\alpha^1\Sigma_u^+-X^3\Sigma_g^-$	2-0	80000.6	1.653	2.58×10^{-5}	80002	1.640
1221.1Q	"	3-0	81822.4	1.6327	0.7×10^{-5}	81822.7	1.633
1196.4Q	"	4-0	83599.7	1.613	1.0×10^{-5}	83599.6[a]	1.59
1262.1Q	$\beta^3\Sigma_u^+-X^3\Sigma_g^-$	2-0	79228.3	1.665	1.48×10^{-5}	79228	1.65
1233.4Q	"	3-0	81073.4	1.640	2.10×10^{-5}	81072	1.63
1144.6Q	$^3\Sigma_u^+-X^3\Sigma_g^-$	0-0	87369.1	1.706	2.80×10^{-5}		

[a]This value is a newly corrected one. The previous value was 83586.5 cm^{-1}. Private communication of Douglas (see Table I).

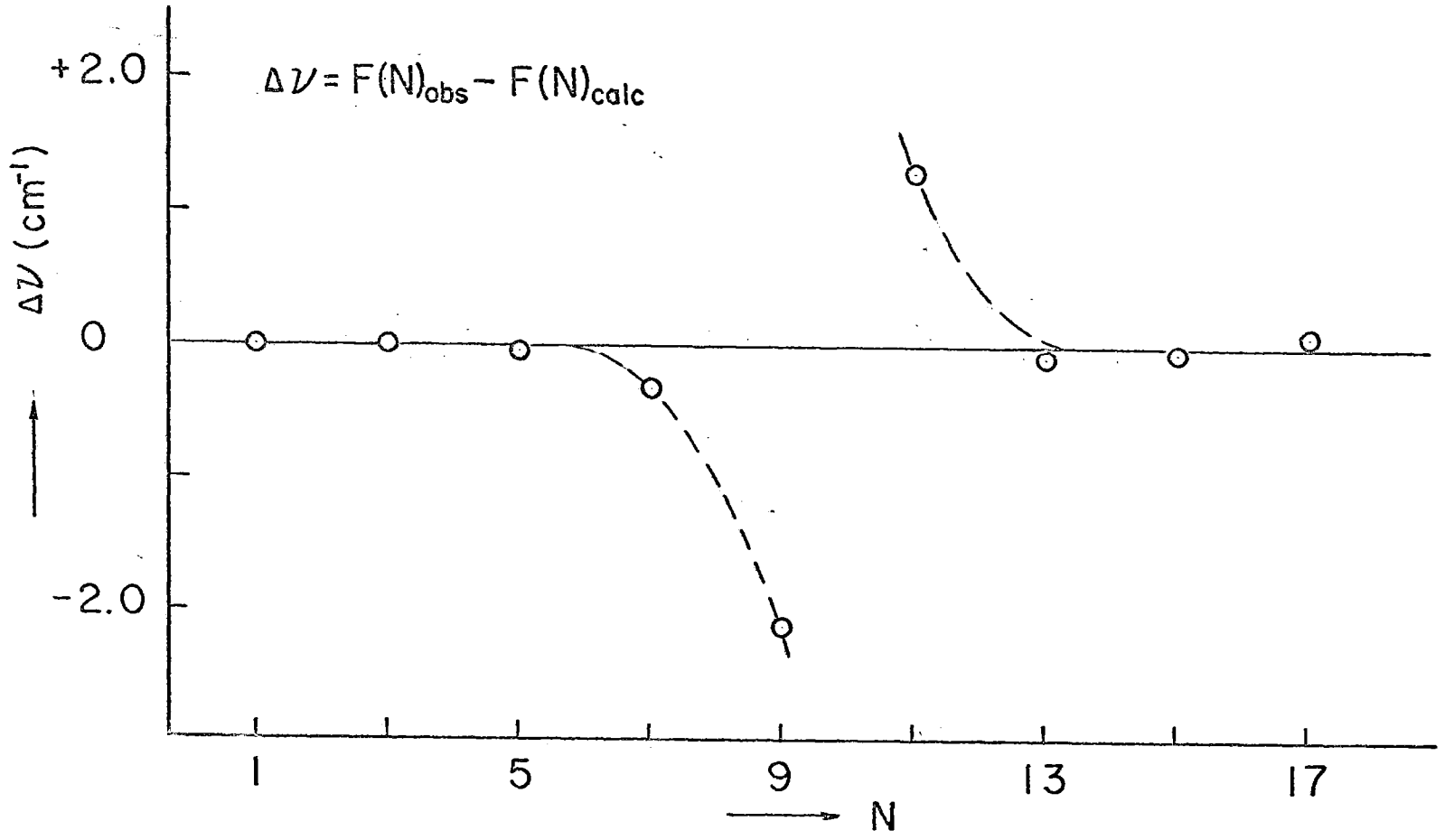


Fig. 2

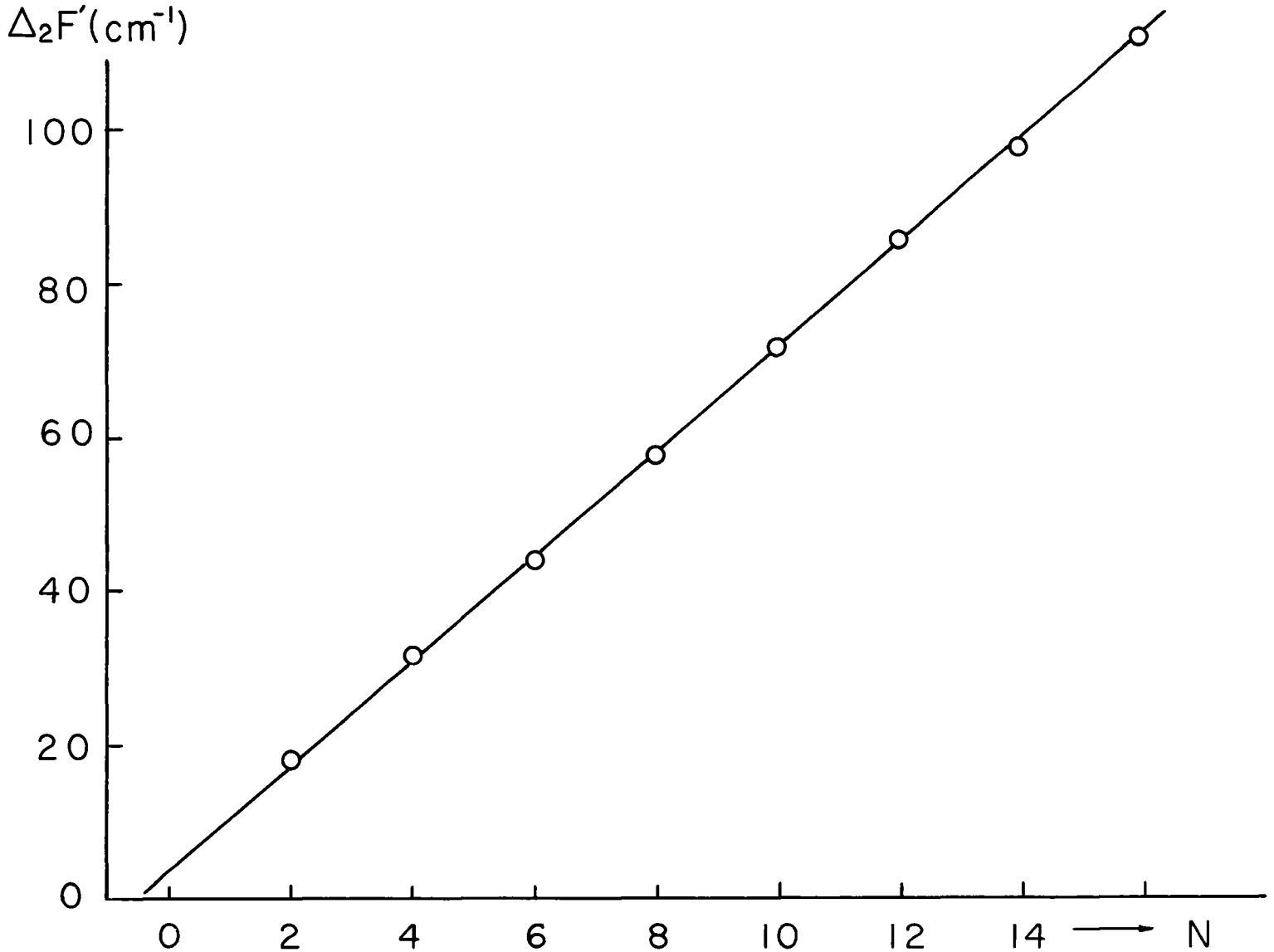


Fig. 3

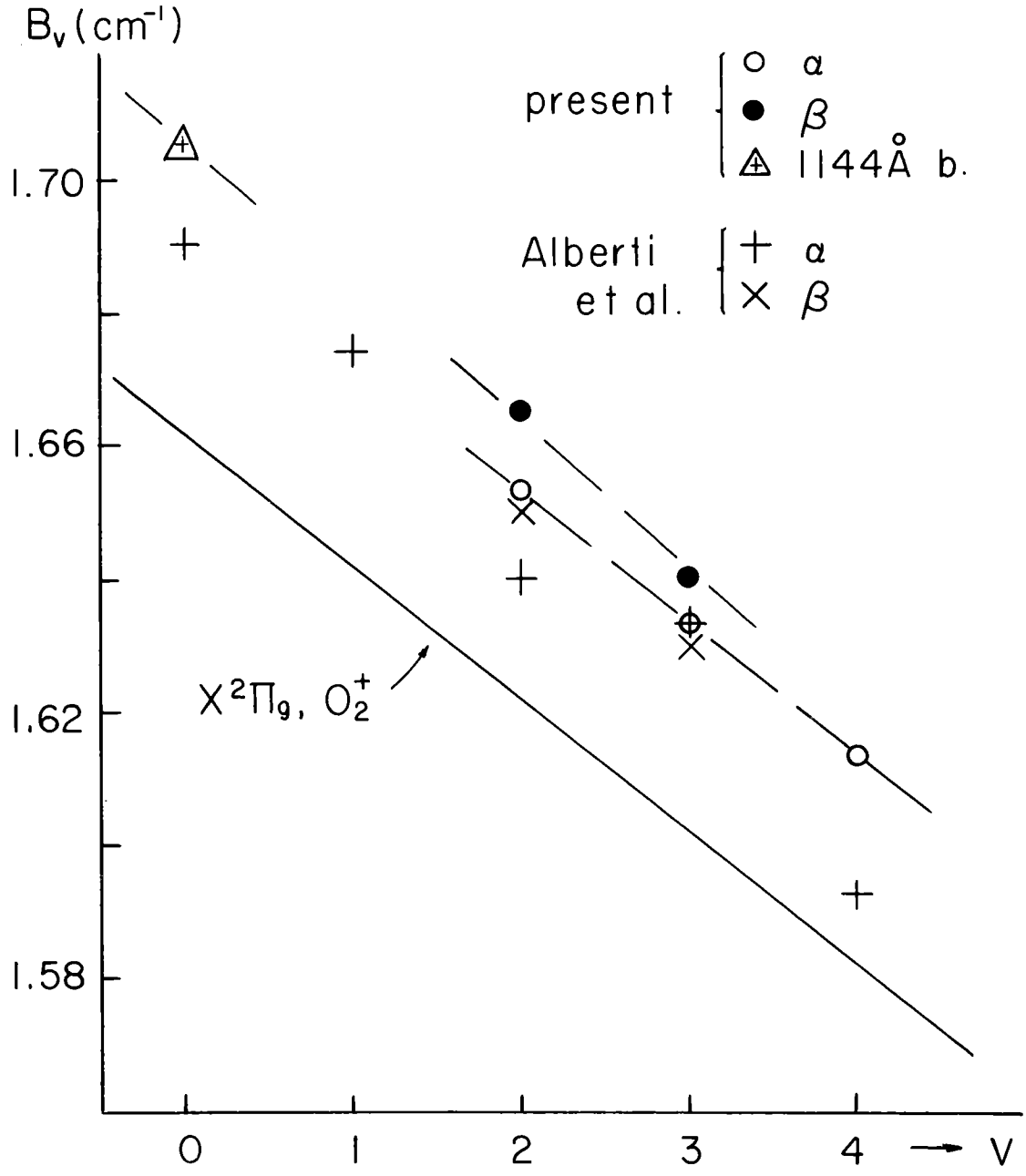

$B_v\,(cm^{-1})$
1.70
1.66
1.62
1.58
present
α
β
1144Å b.
Alberti et al.
α
β
$X^2\Pi_g,\ O_2^+$
0
1
2
3
4
V

Fig. 4